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(54) FLUOROPOLYMER AND ELECTRIC WIRE AND CABLE BOTH COATED WITH THE SAME

(57) Although an electric wire or cable, which is coated with a fluorine-containing polymer comprising tetrafluoroethylene and hexafluoropropylene and, if necessary, perfluoroalkyl vinyl ether, wherein a melt flow rate (MFR) at 372°C is within a range from 0.1 to 100, and the total content (ppm) of an alkali metal and an alkali earth metal does not exceed the value obtained by calculating from the melt flow rate (MFR) at 372°C according to the formula (1):

$$5.2 \times e^{0.125(\text{MFR})} + 2 \quad (1)$$

and exceeds the value obtained by calculating accord-

ing to the formula (2):

$$0.35 \times e^{0.125(\text{MFR})} \quad (2)$$

contains the alkali metal or alkali earth metal, electrical characteristics of the coated electric wire are not impaired and a core wire is not corroded.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a fluorine-containing polymer, and an electric wire and cable coated therewith and, more particularly, to a fluorine-containing polymer containing a very small amount of an alkali metal and an alkali earth metal, and an electric wire and cable coated with the polymer.

RELATED ART

[0002] For example, tetrafluoroethylene (TFE)/hexafluoropropylene (HFP) copolymers prepared by the emulsion polymerization contain polymer main chains and polymer terminals which are unstable to heat and a shear force.

[0003] When a polymer having unstable polymer main chains and polymer terminal groups is used as a coating material for electric wire or cable, they are decomposed by heat or a shear force applied during coating to form cells and voids in the coating material and, therefore, a core wire can not be completely coated and insulating performances are lowered.

[0004] The kind of the unstable polymer terminal group varies depending on the polymerization method and the kind of a polymerization initiator and a chain transfer agent. For example, when a conventional persulfate salt (for example, ammonium persulfate, potassium persulfate, etc.) is used as the polymerization initiator in the emulsion polymerization, carboxylic acid terminal groups are formed. It is known that these carboxylic acid terminal groups are a source of a volatile component produced during melting of the polymer.

[0005] Depending on the conditions on melting, groups such as olefin ($-\text{CF}=\text{CF}_2$) and acid fluoride ($-\text{COF}$) are sometimes formed at polymer terminals and these terminal groups can cause cells or voids in a final product of the polymer.

[0006] To solve these problems of cells or voids in the polymer caused by unstable main chains or unstable terminal groups, U.S. Patent No. 3,085,083 has proposed a method of stabilizing the unstable terminal groups by bringing a fluorine-containing polymer into contact with water at a temperature within a range from 200°C to 400°C (wet heat treatment), while Japanese Kokoku (Examined) Patent Publication No. 5 - 10204 (corresponding to U.S. Patent No. 4,626,587) has proposed a method of reducing the number of unstable main chains of a TFE/HFP copolymer by applying a high shear force to the copolymer in a twin-screw extruder and subjecting the resulting pellets to the fluorination reaction to improve the color tone of the pellets and to stabilize the unstable terminal groups.

[0007] U.S. Patent No. 3,085,083 also describes that a base, a neutral salt or a basic salt, which contains an alkali metal or an alkali earth metal, is added to increase

a reaction rate in a wet heat treatment. When the wet heat treatment is employed as a method for a stabilization treatment of terminals, a base or salt of the alkali metal or alkali earth metal is often added.

[0008] Even if the fluorination reaction is conducted to stabilize terminals as in the latter case, when using potassium persulfate as a polymerization initiator, potassium remains as a residue of the initiator in the polymer.

[0009] However, when a fluorine-containing polymer prepared by using a compound containing an alkali metal or an alkali earth metal (for example, polymerization initiator) or a fluorine-containing polymer post-treated with a compound containing an alkali metal or an alkali earth metal contains a large amount of the alkali metal or alkali earth metal, electrical characteristics of an electric wire or cable coated with the fluorine-containing polymer are likely to be impaired and a core wire is likely to be corroded.

SUMMARY OF THE INVENTION

[0010] Thus, an object of the present invention provides a fluorine-containing polymer, which does not impair electrical characteristics of a coated electric wire and does not corrode a core wire, although it contains an alkali metal or an alkali earth metal, and an electric wire or cable coated with the fluorine-containing polymer.

DETAILED DESCRIPTION OF THE INVENTION

[0011] According to the present invention, the object described above can be achieved by a fluorine-containing polymer comprising 70 to 95% by weight of tetrafluoroethylene, 5 to 25% by weight of hexafluoropropylene and 0 to 20% by weight of perfluoroalkyl vinyl ether, wherein a melt flow rate (MFR) (g/10 min., ASTM D2116) at 372°C is within a range from 0.1 to 100, and the total content (ppm) of an alkali metal and an alkali earth metal does not exceed the value obtained by calculating from the melt flow rate (MFR) at 372°C according to the formula (1):

$$5.2 \times e^{0.125(\text{MFR})} + 2 \quad (1)$$

and exceeds the value obtained by calculating according to the formula (2):

$$0.35 \times e^{0.125(\text{MFR})} \quad (2),$$

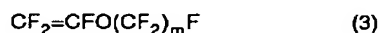
and by an electric wire or cable coated with the fluorine-containing polymer.

[0012] Regarding the electric wire or cable, which is coated with a fluorine-containing polymer wherein the

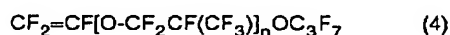
total content (ppm) of an alkali metal and an alkali earth metal exceeds the value obtained by calculating according to the above formula (1), electrical characteristics are likely to be impaired and a core wire is likely to be corroded. On the other hand, in the case of a fluorine-containing polymer wherein the total content does not exceed the value obtained by calculating according to the above formula (2), unstable terminal groups are not sufficiently stabilized.

[0013] The fluorine-containing polymer used in the present invention is, for example, a copolymer comprising at least two monomers selected from the group consisting of tetrafluoroethylene, hexafluoropropylene and perfluoroalkyl vinyl ether.

[0014] The perfluoroalkyl vinyl ether is a vinyl ether represented by the formula (3):



wherein m is an integer of 1 to 6, or a vinyl ether represented by the formula (4)



wherein n is an integer of 1 to 4.

[0015] When the fluorine-containing polymer to be treated is a tetrafluoroethylene/hexafluoropropylene copolymer (FEP), the copolymer preferably comprises 72 to 96% by weight of tetrafluoroethylene and 4 to 28% by weight of hexafluoropropylene. When the fluorine-containing polymer is a tetrafluoroethylene/perfluoroalkyl vinyl ether copolymer (PFA), the copolymer preferably comprises 92 to 99% by weight of tetrafluoroethylene and 1 to 8% by weight of perfluoropropyl vinyl ether. When the fluorine-containing polymer is a copolymer of tetrafluoroethylene and a plurality of perfluoroalkyl vinyl ethers (MFA), the copolymer preferably comprises 84 to 99.45% by weight of tetrafluoroethylene, 0.5 to 13% by weight of perfluoromethylvinyl ether, and 0.05 to 3% by weight of perfluoroalkyl vinyl ether having alkyl other than methyl, such as perfluoropropyl vinyl ether.

[0016] These polymers may be prepared by copolymerizing the other monomer in such amount that essential properties of each polymer are not impaired. Examples of the other monomer include hexafluoropropylene, perfluoroalkyl vinyl ether, ethylene, vinylidene fluoride and chlorotrifluoroethylene.

[0017] The fluorine-containing polymer is preferably prepared by the emulsion polymerization or suspension polymerization, particularly the emulsion polymerization. The polymerization conditions are the same as those in the case of the conventional emulsion polymerization or suspension polymerization, except that the amount of the compound containing the alkali metal or alkali earth metal (for example, a polymerization initia-

tor, a chain transfer agent, a dispersant, etc.) is controlled so that the amount of the alkali metal or alkali earth metal does not exceed the total content thereof to be contained in the resulting polymer.

[0018] In the post-treatment of the resulting fluorine-containing polymer, for example, before or after the step of drying the fluorine-containing polymer or during the extrusion step, even when using the compound containing the alkali metal or alkali earth metal, the amount must be controlled so that the total amount of the alkali metal or alkali earth metal in the fluorine-containing polymer is within the above defined range.

[0019] More preferably, the total content (ppm) of the alkali metal or alkali earth metal in the fluorine-containing polymer does not exceed the value obtained by calculating from the melt flow rate (MFR) (g/10 min., ASTM D2116) at 372°C according to the formula (5):

$$1.3 \times e^{0.125(\text{MFR})} + 2 \quad (5)$$

and exceeds the value obtained by calculating according to the formula (6):

$$0.7 \times e^{0.125(\text{MFR})} \quad (6)$$

[0020] Specific examples of the alkali metal or alkali earth metal include hydroxides such as potassium hydroxide or sodium hydroxide, carbonate salts such as potassium carbonate or calcium carbonate, sulfate salts such as potassium sulfate, or nitrate salts such as potassium nitrate.

[0021] The fluorine-containing polymer of the present invention does not substantially have unstable terminal groups.

[0022] Preferably, $-\text{CF}_2\text{H}$ accounts for at least half of polymer chain terminals and substantially all polymer chain terminals comprise $-\text{CF}_2\text{H}$, or $-\text{CF}_2\text{H}$ and $-\text{CH}_3$. As used herein, the expression "does not substantially have unstable terminal groups" refers to the state that the number of unstable terminal groups such as COOH , $-\text{COF}$ and $-\text{CF}=\text{CF}_2$ is at most 20 per 10^6 carbon atoms of the polymer.

[0023] When the fluorine-containing polymer is a tetrafluoroethylene/hexafluoropropylene copolymer (FEP), a tetrafluoroethylene/perfluorovinyl ether polymer (PFA), a copolymer of tetrafluoroethylene/hexafluoropropylene/perfluoroalkyl vinyl ether, or a copolymer of tetrafluoroethylene, perfluoromethyl vinyl ether and perfluoroalkyl vinyl ether having alkyl other than methyl, such as perfluoropropyl vinyl ether, it may have a melt viscosity of 0.1 to 100 kPa·s at 372°C.

[0024] The coated electric wire or cable can be produced in the same method of producing an electric wire and cable by coating with a conventional fluororesin, except that the fluorine-containing polymer described

above is used as the coating material.

[0025] The kind of the electric wire or cable is not specifically limited. The core wire may be a single core, a strand wire, or a coaxial cable. In the case of the coaxial cable, the fluorine-containing polymer used in the present invention can also be used as an internal insulating material.

PREFERRED EMBODIMENTS OF THE INVENTION

[0026] The following Examples and Comparative Examples further illustrate the present invention.

[0027] Physical properties were determined by the following procedures.

(1) Melt flow rate (MFR)

[0028] A melt flow rate (g/10 min.) was measured at 372°C in accordance with ASTM D2116.

(2) Dielectric dissipation factor

[0029] A dielectric dissipation factor was measured by a standing wave method using a coaxial cable in accordance with ASTM D2520.

Example 1

[0030] By the emulsion polymerization method (polymerization pressure: 4.2 MPa, polymerization temperature: 95°C, initiator: ammonium persulfate (APS), emulsifier: $C_7F_{15}COONH_4$), a tetrafluoroethylene/hexafluoropropylene copolymer (hexafluoropropylene content: 10.0% by weight, MFR = 5) was polymerized and then coagulated by adding nitric acid after the polymerization. After dehydration and drying, an 1 wt% aqueous potassium carbonate solution was added to the polymer so that a potassium content was 4 ppm (the amount was measured by atomic adsorption spectrometry). After dispersing by a powder mixer, the dispersion was dried again and extruded into pellets in a twin-screw extruder. During the extrusion, water and air were fed (extrusion amount: 50 kg/hour, water: 5.5 kg/hour, air: 50 NL/min.) in the extruder to stabilize polymer terminals by the wet heat treatment.

[0031] The structure of the polymer terminals after the treatment was analyzed by a Fourier transform infrared spectroscopy. As a result, those other than $-CF_2H$ terminal groups were not detected.

[0032] The dielectric dissipation factor was measured at 500 MHz. As a result, it was 6.10×10^{-4} .

Example 2

[0033] In the same manner, the dielectric dissipation factor of a tetrafluoroethylene/hexafluoropropylene copolymer (hexafluoropropylene content: 12.0% by weight, MFR = 10), which was obtained in the same

manner as in Example 1 except that the proportion of the monomer was changed and the content of potassium was changed to 6 ppm, was measured. As a result, it was 6.53×10^{-4} .

Comparative Example 1

[0034] The dielectric dissipation factor of a polymer, which was treated in the same manner as in Example 1 except that the content of potassium was changed to 70 ppm, was measured. As a result, it was 8.94×10^{-4} .

Comparative Example 2

[0035] The dielectric dissipation factor of a polymer, which was treated in the same manner as in Example 2 except that the content of potassium was changed to 100 ppm, was measured. As a result, it was 9.95×10^{-4} .

Example 3

[0036] Using a tetrafluoroethylene/hexafluoropropylene copolymer (hexafluoropropylene content: 13.5% by weight, MFR = 17, potassium content: 10 ppm) obtained in the same manner as in Example 1, coated electric wires each having a wire size (core material of copper) of 511 μm (20.1 mil) and a coating thickness of 196 μm (7.7 mil) were produced. These coated electric wires were produced by molding at a rate of 305 m/min (1000 ft/min) using a single-screw extruder having a diameter of 5.1 cm (2 inch).

[0037] After standing at room temperature for 10 days, a coated portion was peeled off and a core wire made of copper was visually observed. As a result, discoloration was not observed.

Comparative Example 4

[0038] After a coated electric wire produced by using a copolymer which was obtained in the same manner as in Example 3 except that the content of potassium was changed to 90 ppm, was allowed to stand at room temperature for 10 days, a coated portion was peeled off and a core wire made of copper was visually observed. As a result, partial discoloration (considered to be caused by corrosion of copper) was observed.

Claims

1. A fluorine-containing polymer comprising 70 to 95% by weight of tetrafluoroethylene, 5 to 25% by weight of hexafluoropropylene and 0 to 20% by weight of perfluoroalkyl vinyl ether, wherein a melt flow rate (MFR) (g/10 min., ASTM D2116) at 372°C is within a range from 0.1 to 100, and the total content (ppm) of an alkali metal and an alkali earth metal does not exceed the value ob-

tained by calculating from the melt flow rate (MFR)
at 372°C according to the formula (1) :

$$5.2 \times e^{0.125(\text{MFR})} + 2 \quad (1) \quad 5$$

and exceeds the value obtained by calculating according to the formula (2):

$$0.35 \times e^{0.125(\text{MFR})} \quad (2). \quad 10$$

2. A fluorine-containing polymer wherein -CF₂H accounts for at least half of polymer chain terminals and substantially all polymer chain terminals comprise -CF₂H, or -CF₂H and -CH₃. 15
3. An electric wire or cable coated with a fluorine-containing polymer wherein the total content (ppm) of an alkali metal and an alkali earth metal does not exceed the value obtained by calculating from a melt flow rate (MFR) (g/10 min., ASTM D2116) at 372°C according to the formula (1) : 20

$$5.2 \times e^{0.125(\text{MFR})} + 2 \quad (1) \quad 25$$

and exceeds the value obtained by calculating according to the formula (2):

$$0.35 \times e^{0.125(\text{MFR})} \quad (2). \quad 30$$

4. The electric wire or cable according to claim 3, wherein -CF₂H accounts for at least half of polymer chain terminals and substantially all polymer chain terminals comprise -CF₂H, or -CF₂H and -CH₃. 35
5. The electric wire or cable according to claim 3, wherein the fluorine-containing polymer is a fluorine-containing polymer prepared by emulsion polymerization. 40
6. The electric wire or cable according to anyone of claims 3 to 5, wherein the fluorine-containing polymer is a copolymer comprising at least two monomers selected from the group consisting of tetrafluoroethylene, hexafluoropropylene and perfluoroalkyl vinyl ether. 45
7. The electric wire or cable according to anyone of claims 3 to 6, wherein the contained alkali metal and alkali earth metal comprise at least one of potassium and sodium. 50

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/06048

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.⁷ C08F14/26, C08F8/06, C08L27/18, C08K3/18,
C08K3/28//H01B3/44, H01B7/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl.⁷ C08F14/26, C08F8/06, C08L27/18, C08K3/18,
C08K3/28//H01B3/44, H01B7/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DERWENT WPI/L "unstable(w) fraction" in abstract

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP, 789038, A1 (E.I. DU PONT DE NEMOURS AND COMPANY), 13 June, 1997 (13.06.97), Claims: page 3, lines 46 to 59; example 5 & JP, 09-202814, A, Claims; Par. No. 0018; example 5	1-7
X	EP, 648787, A1 (AUSIMONT S.p.A.), 19 April, 1995 (19.04.95), Claims: page 3, lines 5 to 12 & JP, 07-179508, A, Claims; Par. No. 0012	1-2 3-7
X	US, 3969435, A (E.I. Du Pont De Nemours and Company), 13 July, 1976 (13.07.76), Claims; Column 7, lines 1 to 7 & JP, 51-122155, A, Claims; page 9, upper left column, lines 1 to 6	1-7
Y	JP, 10--17621, A (Asahi Glass Co., Ltd.), 20 January, 1998 (20.01.98), Claims; example (Family: none)	1-7
Y	JP, 11-210941, A (Asahi Glass Co., Ltd.), 06 August, 1999 (06.08.99),	1-7

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
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 "O" document referring to an oral disclosure, use, exhibition or other means
 "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
 "Z" document member of the same patent family

Date of the actual completion of the international search
30 November, 2000 (30.11.00)Date of mailing of the international search report
12 December, 2000 (12.12.00)Name and mailing address of the ISA/
Japanese Patent Office

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/06048

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Claims; example (Family: none) US, 3085083, A (E.I. Du Pont De Nemours and Company), 09 April, 1963 (09.04.63), Claims	1-7

Form PCT/ISA/210 (continuation of second sheet) (July 1992)